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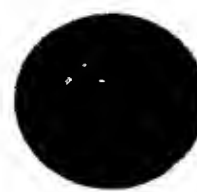
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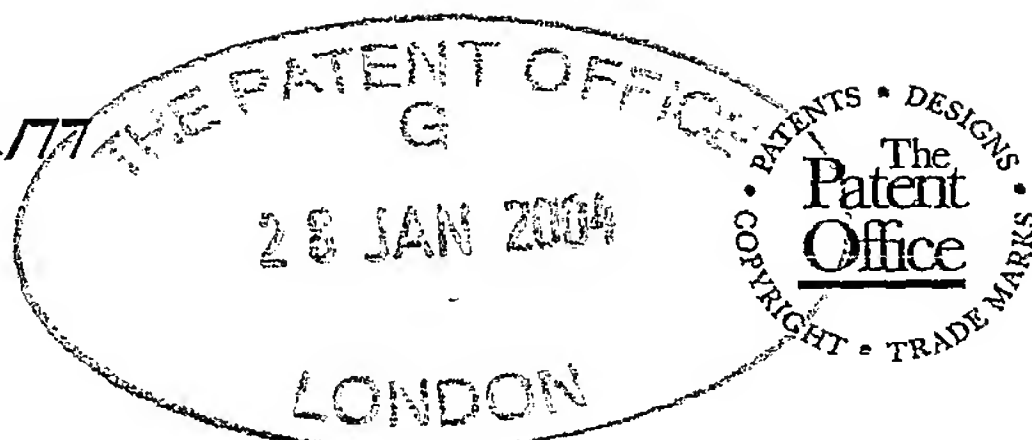
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Patents ADP number (if you know it)			
If the applicant is a corporate body, give the country/state of its incorporation	8147845001 A/L 26/2/04 GB		
4. Title of the invention	Improved Polymer Composition		
5. Name of your agent (if you have one)	J. A. KEMP & CO.		
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J.A. KEMP & CO.

Date 28 January 2004

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IMPROVED POLYMERIC COMPOSITION

The present invention relates to polymeric compositions for a variety of uses.

It is well known that many polymeric compositions are adversely affected by
 5 light, in particular UV light. This can result in a variety of physical properties of the
 composition being affected. Typically, solid plastics compositions have their
 strength adversely affected so that, over time, they become more brittle. Similar
 comments apply to coating compositions. Other properties which can be adversely
 affected include colour. It is well known, for example, that coating compositions
 10 such as paints are adversely affected by light so that fading or, in the case of white
 formulations, yellowing occurs.

Various attempts have been made to counteract these adverse effects. This
 has included incorporating light stabilisers into the composition, typically hindered
 amines. However, incorporation of such light stabilisers is relatively expensive and
 15 not always particularly effective.

The present invention resides in the discovery that the incorporation of
 particular types of titanium dioxide and zinc oxide can effectively counteract the
 adverse effect of exposure to light, typically sun light.

In our GB Application No. 0310365.2 we disclose that the degradation of
 20 polymeric compositions can be retarded if the compositions also have present either
 zinc oxide or titanium dioxide which has been doped with a second element or
 reduced zinc oxide. In other words by using these doped materials or reduced zinc
 oxide rather than ordinary titanium dioxide or zinc oxide it is, for example, possible
 either to provide a polymeric composition which gives better protection against UV
 25 light or a composition having the same resistance to degradation but containing a
 smaller quantity of light stabiliser. The application thus describes a polymeric
 composition which comprises an amount of one or more organic or inorganic
 components which are photosensitive and/or which are degraded by another
 ingredient of the composition, and an amount of either TiO_2 and/or ZnO which has
 30 been doped with a second element or reduced ZnO , this composition having a rate of

deterioration of a UV light-sensitive physical factor at least 5% less than that of a composition having the same formulation except that it does not contain the TiO_2 and/or ZnO which has been doped with a second element or reduced ZnO .

By a "physical factor" is meant a measurable value of a physical property of the composition which is adversely affected by UV light. Examples of such physical factors include degradation and, in consequence, strength, colour change (e.g. for paints and textiles) and photographic stability (e.g. for photographic films).

Thus if the rate of deterioration of a physical factor is X then the amount of the component(s) which are photosensitive and/or which are degraded by another ingredient of the composition, possesses a said rate of deterioration of Y where Y is greater than X by at least 5%, and the amount of doped TiO_2 and/or ZnO and/or reduced ZnO reduces the said rate of loss from Y to X. The present invention also provides the use of a doped TiO_2/ZnO and/or reduced ZnO to reduce the concentration of one or more light stabilisers in a polymeric composition as well as to reduce the rate of deterioration of a physical factor of a polymeric composition. The present invention further provides a method of improving the stability of a physical factor of a composition which comprises one or more components which are photosensitive and/or which are degraded by another ingredient of the composition which comprises incorporating into the composition a doped TiO_2/ZnO and/or reduced ZnO .

It has now been found, according to the present invention, that the way in which the oxide is doped has a material effect on the efficacy of the oxide. Indeed it has now been appreciated that it is important that if the oxide is to be really effective there must be dopant on its surface which can interact with the component of the composition to be protected. For example if, in a two phase composition, the oxide is present in the hydrophilic phase and the component to be protected is in the hydrophobic phase there is little interaction because of the phase boundary e.g. in a paint or coating. Thus the free radicals generated by degradation of the component cannot contact the dopant without moving from one phase to another. Although existing methods for doping in the bulk will normally also result in some dopant in or

on the surface of the particle, it is possible according to the present invention to use materials which are only surface doped i.e. where there is dopant only in or on the surface of the particle. In one embodiment such materials may be used in a single phase formulation

5

Accordingly the present invention provides (although not dependant on the above theory) a composition which comprises an amount of one or more organic or inorganic components which are photosensitive and/or which are degraded by another ingredient of the composition and an amount of TiO_2 and/or ZnO which has
10 been doped at least on or in a surface thereof with one or more other elements, typically with one i.e with only a second element.

The composition may be polymeric, which as used herein means that the composition may comprise one or more polymeric materials, typically constituting at least 1%, preferably 5% by weight of the composition.. Also, the composition may
15 be solid or liquid. Where a polymeric material is present it may comprise at least part of the organic component and/or it may comprise a binder and/or other component of the composition.

Where the particle has been bulk doped there will, in general, be dopant throughout the particle. On the other hand where the particle has been "surface
20 doped" (i.e. the dopant is only in or on the surface) there will be a concentration gradient e.g. such that the ratio of dopant atoms to titanium or zinc atoms at the surface or outmost "skin" of the particle is greater than the ratio in the core or centre where it may be zero. In general, the composition has a formulation which has a rate of deterioration of a UV light-sensitive physical factor at least 5% less than that of a
25 composition having the same formulation except that it does not contain the said TiO_2 and/or ZnO which has been doped with a second element.

By "a polymeric composition" as used herein is meant a composition which comprises one or more polymeric materials. The composition can be solid or liquid.

In some instances, the composition of the present invention will contain TiO_2
30 and/or ZnO which has not been doped. Typically such undoped TiO_2/ZnO will be

present as pigment, generally having a particle size of at least 100 nm.

Typical solid materials include polymeric solids including three dimensional objects, films and fibres as well as textiles and fabrics e.g. clothing and netting made from woven and non-woven fibres as well as foamed articles; solids which are not fibres are sometimes preferred. Three-dimensional objects include those made by melt-forming processes including extruded and moulded articles. Typical articles to which the present invention may be applied include generally external household and building materials including blinds and plastics curtains, trellis, pipes and guttering, cladding and facings such as soffit board and plastics roofing material which can be profiled as with corrugated sheeting, doors and windows frames. Other articles include advertising hoardings and the like e.g. advertising boards on vehicle sides as well as vehicle bodies and body parts including bumpers for cars, buses and trucks as well as roofs which can be used also for boats, as well as superstructures and hulls for boats and also bodies for lawnmowers and tractors and yachts, along with containers such as bottles, cans, drums, buckets and oil and water storage containers. Other objects include garden furniture. In one embodiment the solids are not transparent.

Films to which the present invention can be applied include self supporting as well as non-self supporting films such as coatings. Self-supporting films to which the present invention applies include photographic films, packaging film and plastics film bearing indicia, typically as advertising film, which can also be applied over advertising hoardings. Such films can contain one or more customary ingredients for such products. Thus photographic film will contain one or more dyes or dye couplers and, optionally, a silver halide.

In some instances the polymeric composition itself is not liable to degradation but the composition is intended to protect a substrate or, in the case of a container, something placed in it. Thus such compositions can contain the doped TiO_2/ZnO . Examples include pigmented and non-pigmented containers, typically bottles.

Accordingly, the present invention also provides a self-supporting polymer composition, or a varnish composition, intended to protect a composition adjacent

thereto from the adverse effects of light, and which comprises TiO_2 and/or ZnO which has been surface doped with at least a second element. In one embodiment the composition is 3-dimensional and comprises a surface layer with the TiO_2 and/or ZnO while the non-surface part is generally not wood or a reconstituted wood such as chipboard, plywood or fibreboard and is preferably synthetic.

Coating compositions are typically paints and varnishes which contain a polymer either as the active ingredient as in some varnishes or as a support as in paints along with furniture polishes, waxes and creams; they can be aqueous or non aqueous i.e. contain an organic solvent in which case they can be mono-phase or poly-phase, typically as an oil-in-water or water-in-oil emulsion. This coating composition can be in the form of a waterproofing agent. These coating compositions can contain one or more customary ingredients for such products. Some cosmetics compositions contain one or more polymers; such compositions are less preferred in the present invention.

The polymers which can be used in the compositions of the present invention include natural and synthetic polymers which may be thermoplastic or thermosetting.

The suitable polymers which may be homopolymers or copolymers which can be random, block or graft copolymers; the polymers can be crosslinked. Such polymers may be saturated or unsaturated. Typical polymers include alkylene polymers such as ethylene and propylene polymers, typically homopolymers, including polyethylene foams, siloxane and sulphide polymers, polyamides such as nylon, polyesters, such as PET, acrylate and methacrylate polymers e.g. poly(methyl methacrylate), polyurethanes, including foams, vinyl polymers such as styrene polymers e.g. ABS, including polystyrene foam, vinyl chloride polymers and polyvinyl alcohol as well as engineering thermoplastics including aromatic polymers, e.g. polymers such as linear aromatic semi-crystalline polymers such as PEEK and PES. Fluorinated polymers such as PTFE and polyvinylidene fluoride can be used. The polymers can be thermosetting as with epoxy resins as well as phenolic, urea, melamine and polyester resins

Natural polymers which can be used include cellulosic polymers, as in paper

including starch, polysaccharides, lignins, and polyisoprenes such as natural rubbers.

It will be appreciated that some polymers can be regarded as photostable in that there is no, or no significant, change in physical characteristics on exposure to UV light. These polymers are, therefore, not photosensitive and their use does not
5 fall within the scope of the present invention.

Typical polymers for different applications include the following: (a) polyester, polyamide e.g. nylon, acrylics for fibres and fabrics; (b) polyester, polyvinyl chloride, polyethylene, polypropylene for bottles and the like; (c) polyethylene, polypropylene, polyvinyl chloride for film (non active such as
10 packaging).

The compositions can contain the usual additional ingredients characteristic for the composition in question including inorganic and organic pigments, including "ordinary" TiO_2 and/or ZnO , fillers and extenders as well as light stabilisers, typically hindered amine stabilisers. The additional ingredients may themselves be
15 susceptible to attack, with the degraded components potentially causing degradation of the polymer or other component of the composition.

The rate of colour change can be determined by illuminating a sample of the composition with and without the doped TiO_2 or ZnO with sunlight or visible light and measuring the spectral response of the composition over a given period and
20 determining the change in wavelength emitted. Accelerated ageing tests using, for example a Fadeometer, can be used for this purpose.

The rate of loss of strength of an article of the present invention can be determined in a similar manner by measuring tensile properties such as elongation at break or Young's modulus, using standard equipment such as an Instron tester; again
25 an accelerated ageing procedure is beneficial.

While any reduction in the wavelength change or other physical factor is an advantage, it is generally desirable that the presence of the doped oxide should reduce the rate of change by an amount of at least 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

30 It will be appreciated that although it will normally be the case that the bulk

dopant will be the same element as the or each surface dopant (for simplicity of preparation), this need not necessarily be the case. (Of course with reduced zinc oxide there is no bulk dopant.) By this means it is possible, for example, to modify the colour of the particles. Suitable dopants for the oxide particles include

5 manganese, which is especially preferred, e.g. Mn^{2+} but also Mn^{3+} , vanadium, for example V^{3+} or V^{5+} , chromium and iron but other metals which can be used include nickel, copper, tin, especially Sn^{4+} ; aluminium, lead, silver, zirconium, zinc, cobalt, especially Co^{2+} , gallium, niobium, for example Nb^{5+} , antimony, for example Sb^{3+} , tantalum, for example Ta^{5+} , strontium, calcium, magnesium, barium, molybdenum,

10 for example Mo^{3+} , Mo^{5+} or Mo^{6+} as well as silicon. These metals can be incorporated singly or in combinations of two or three or more. It will be appreciated that for effective bulk doping the size of the ion must be such as can readily be inserted into the crystal lattice of the particle. For this purpose Mn^{3+} , vanadium, chromium and iron are generally the most effective; the ionic size of Mn^{2+} is much larger than that

15 of Ti^{4+} and so there is little probability of ionic diffusion of Mn^{2+} into the TiO_2 crystal lattice. On the other hand there is no such size limitation for the elements used in surface doping; preferred surface dopants include manganese, eg. as Mn^{2+} , cerium, selenium, chromium and iron.

The optimum total amount of the second component on, and, if present, in,

20 the particle may be determined by routine experimentation but it is preferably low enough so that the particles are minimally coloured. Amounts as low as 0.1 mole % or less, for example 0.05 mole %, or as high as 1 mole % or above, for example 5 mole % or 10 mole %, can generally be used. Typical concentrations are from 0.5 to 2 mole % by weight. The mole ratio of dopant to host metal on the surface is

25 typically from 2-25:98-75, usually 5-20:95-80 and especially 8-15:92-85. The amount of dopant at the surface can be determined by, for example, X-ray Photoelectron Spectroscopy (XPS).

The surface-doped particles can be obtained by any one of the standard processes for preparing such doped oxides and salts. These include techniques such

30 as those described below. It will be appreciated that the dopant need not necessarily

be present as an oxide but as a salt such as a chloride or a salt of an oxygen-containing anion such as perchlorate or nitrate. However bulk doping techniques will generally result in some surface doping as well and these techniques can be used in the present invention. Such techniques include a baking technique by combining
5 particles of a host lattice (TiO_2/ZnO) with a second component in the form of a salt such as a chloride or an oxygen-containing anion such as a perchlorate or a nitrate, in solution or suspension, typically in solution in water, and then baking it, typically at a temperature of at least 300°C . Other routes which may be used to prepare the doped materials include a precipitation process of the type described in J. Mat. Sci. (1997)
10 36, 6001-6008 where solutions of the dopant salt and of an alkoxide of the host metal (Ti/Zn) are mixed, and the mixed solution is then heated to convert the alkoxide to the oxide. Heating is continued until a precipitate of the doped material is obtained. Further details of preparation can be found in WO 00/60994 and WO 01/40114.

It will be appreciated that such baking techniques and the like will result in
15 dopant in the surface forming part of the crystal lattice, while in other techniques the dopant will merely be adsorbed, or remain as a separate layer, on the particle surface. It is thought likely that if the dopant is to quench internally generated free radicals then it needs to be in the crystal lattice.

The rutile form of titania is known to be less photoactive than the anatase
20 form and is therefore preferred. Zinc oxide can be in the form of reduced zinc oxide particles (i.e. particles which possess an excess of zinc ions relative to the oxygen ions).

Doped TiO_2 or doped ZnO may be obtained by flame pyrolysis or by plasma routes where mixed metal containing precursors at the appropriate dopant level are
25 exposed to a flame or plasma to obtain the desired product.

Further details of such particles can be found in WO 99/60994.

The average primary particle size of the particles is generally from about 1 to 200 nm, for example about 1 to 150 nm, preferably from about 1 to 100 nm, more preferably from about 1 to 50 nm and most preferably from about 20 to 50 nm. Since
30 the scavenging effect is believed to be essentially catalytic it is desirable that the

particles are as small as possible to maximise their surface area and hence the area of doped material on the surface. This small size has the advantage that less dopant is needed, which has the consequential advantage that any colouring effect caused by the dopant is reduced.

5 Where particles are substantially spherical then particle size will be taken to represent the diameter. However, the invention also encompasses particles which are non-spherical and in such cases the particle size refers to the largest dimension.

10 The oxide particles used in the present invention may have an inorganic or organic coating. For example, the particles may be coated with oxides of elements such as aluminium, zirconium or silicon, especially silica or, for example, aluminium silicate. The particles of metal oxide may also be coated with one or more organic materials such as polyols, amines, alkanolamines, polymeric organic silicon compounds, for example, $\text{RSi}[\{\text{OSi}(\text{Me})_2\}_x\text{OR}^1]_3$ where R is C_1 - C_{10} alkyl, R^1 is methyl or ethyl and x is an integer of from 4 to 12, hydrophilic polymers such as
15 polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants such as, for example, TOPO. If desired the surface doping can be carried out by a coating technique either separately or in combination with the inorganic or organic coating agent. Thus for example the undoped oxide can be coated with, say, manganese oxide along with an organic or inorganic coating agent such as silica. It is
20 generally unnecessary to coat the oxide particles to render them hydrophilic so that for the aqueous phase the particles can be uncoated. However if the particles are to be in the organic or oily phase their surface needs to be rendered hydrophobic or oil-dispersible. This can be achieved by the application directly of, for example, a suitable hydrophobic polymer or indirectly by the application of a coating, for
25 example of an oxide such as silica (which imparts a hydrophilic property) to which a hydrophobic molecule such as a metal soap or long chain (e.g. C_{12} - C_{22}) carboxylic acid or a metal salt thereof such as stearic acid, a stearate, specifically aluminium stearate, aluminium laurate and zinc stearate.

30 It should be understood that the term "coating" is not to be construed as being limited to a complete covering. Indeed it is generally beneficial for the coating not to

be complete since the coating can act as a barrier to the interaction of the free radicals with the dopant on or in the surface of the particle. Thus it is preferred that the coating should be discontinuous where maximum scavenging effect is desired.

However it will be appreciated that dopant on the surface can still act to quench free radicals generated within the particle in which case the coating can be continuous. Since coatings of silanes and silicones which can be polymeric or short chain or monomeric silanes are generally continuous these are generally less preferred. Thus coating with an inorganic oxide is generally preferred since these generally do not result in a complete coating on the surface of the particles.

10 Typical coating procedures include the deposition of silica by mixing alkali such as ammonium hydroxide with an orthosilicate, such as tetraethylorthosilicate, in the presence of the particle. Alternatively the particle can first be coated with a silane such as (3-mercaptopropyl) trimethoxy silane (MPS) and then silicate e.g. sodium silicate is added. The silane attaches to the particle surface and acts as a
15 substrate for the silicate which then polymerises to form silica. Similar techniques can be used for other inorganic oxides.

The compositions of the present invention can be single phase, either aqueous (or oily or generally hydrophobic) or multiphase. Typical two-phase compositions comprise oil-in-water or water-in-oil formulations. For single phase compositions
20 the oxide particles must of course be dispersible in that phase. Thus the particles are desirably hydrophilic if the composition is aqueous or hydrophobic if the composition is oil-based. However it may be possible to disperse untreated TiO_2 in the oily phase by appropriate mixing techniques. For two or multi-phase composition the particles must be present in the phase containing the ingredient (or
25 one of those ingredients) to be protected. It can, though, be desirable for the particles to be present in both aqueous (or generally hydrophilic) and oily (or generally hydrophobic) phases even if no ingredients which are to be protected are present in one of those phases. Desirably, the weight ratio of the water-dispersible particles to the oil-dispersible particles is from 1:4 to 4:1, preferably from 1:2 to 2:1 and ideally
30 about equal weight proportions.

In the compositions the metal oxides are preferably present at a concentration of about 0.5 to 20 % by weight, preferably about 1 to 10 % by weight and more preferably about 3 to 8 % by weight.

The following Examples further illustrate the present invention.

5 Example 1

Acid Extraction of Manganese Doped Titania

Samples of manganese doped titania were soaked in 25% hydrochloric acid for various times at room temperature. The titania was settled by centrifugation and the supernatant liquid transferred to a 50ml volumetric flask. The titania was washed
10 once by re-suspension in water with the aid of ultrasonics, and again centrifuged. The washings were added to the volumetric flask and the contents made to 50 ml. with de-ionised water.

Samples of the extracts, together with the original powder samples, were analysed for manganese. The water extracts were analysed directly by Atomic
15 Absorbtion Spectroscopy (AAS). The powders were similarly analysed, after digestion with a hydrofluoric acid-sulphuric acid mixture.

DPPH (Radical Scavenging) Assay.

A stock solution of 1mM DPPH in MeOH was made. Samples containing 120µl of DPPH (1mM) plus 300µl TiO₂ (3 mg/ml) were made up to 3ml with MeOH
20 and were placed in a 10 mm quartz cuvette. DPPH is a stable radical, which absorbs at 520nm, therefore a loss of absorbance at this wavelength, is a measure of the radical scavenging ability of the TiO₂. The titania samples were taken from the above series of extractions. The samples were kept in the dark and the absorbance at 520 nm measured every 5 minutes. The samples required mixing before each
25 measurement was taken in order to redisperse the TiO₂.

Time of exposure (hrs)	Extracted Mn (%)	Rate of loss of DPPH (mAbs/min)
0	0	3.4
0.25	3.22	2.05
1.5	4.58	1.6
48	26.0	0.35

- It is clear from these data that 74% of the manganese remained after 48 hours. As the rate of loss of DPPH is then very small it is clear that it is the remaining 26% of the manganese which is in or on the surface which acts to scavenge free radicals.
- 5 Thus particles having manganese available at the surface will scavenge free radicals.

Example 2

10

Preparation of doped TiO_2

Coprecipitation method

- Distilled water (170 cm^3), conc. HCl (12 cm^3) and propan-2-ol (12 cm^3) were mixed together at room temperature with stirring. The appropriate metal salt at the calculated percentage loading was added to the solution (1 % loading in this case).
- 15 After thorough mixing, titanium isopropoxide (10.4 cm^3) was gradually added using a pipette. A gelatinous precipitate was formed instantly. After the solution became clear it was heated in a water bath. The water bath temperature was slowly increased from room temperature to 328 K over a period of a few hours. The solutions were left overnight. The resulting precipitate was decanted and dried at 353 K and then placed
- 20 in an oven for a few hours at 373 K. The samples were then calcined at either 873 K, initially, and then at 1273 K (to ensure formation of rutile crystals) in air for 3 h. (heating regime 298 Kelvin to the chosen temperature at 200 Kelvin/h, dwell time = 3 h followed by cooling to 298 K at 200 K/h).

25 Absorption method

The appropriate metal salt (1 % loading) was dissolved in methanol along with TiO_2 powder Degussa P25 (0.05 moles ~75% anatase and 25% rutile; surface area $\sim 50 \text{ m}^2/\text{g}$; average particle size $\sim 30 \text{ nm}$). The solution was stirred for a few hours and then the solvent was evaporated to leave TiO_2 powder. The powder was placed in

an oven at 423 K for 2-3 h and later calcined in air at 873 K using the same heating regime as for the co-precipitation method.

EPR

- 5 Electron paramagnetic resonance was carried out at low temperatures (100 K) at the EPSRC EPR facility at Cardiff University.

Mn-doped TiO_2 Coprecipitation method

- 10 Mn(II)-doped TiO_2 samples were prepared via both preparation methods and their EPR spectra obtained. The spectrum of 1 % Mn(II)-doped TiO_2 , made by the coprecipitation route, shows Mn^{4+} occupying a substitutional site and Mn^{2+} occupying an interstitial site.

Mn-doped TiO_2 , Absorption method

- 15 The spectrum of 1 % Mn(II)-doped TiO_2 , made by the absorption method, shows substitutionally incorporated Mn^{4+} and Mn^{2+} substitutionally incorporated. Also there is evidence to suggest surfacial Mn^{2+} .

V(IV) doped TiO_2

- 20 V(IV)-doped TiO_2 samples were prepared via both preparation methods and their EPR spectra obtained. The spectrum of 1 % V(IV)-doped TiO_2 , made by the absorption route, shows a poorly resolved spectrum which is due to V^{4+} ions superimposed on a broad resonance which is probably due to Ti^{3+} ions. The spectrum of 1 % V(IV)-doped TiO_2 , made by the coprecipitation method, shows a well-
25 resolved spectrum of an eightfold hyperfine line resonances due to interaction between magnetic moments of the ^{51}V nucleus with paramagnetic V^{4+} ions which is due to V^{4+} occupying substitutional sites in the TiO_2 matrix.

V(V) doped TiO_2

- 30 V(V)-doped TiO_2 samples were prepared via both methods and their EPR spectra obtained. V(V)-doped TiO_2 samples prepared via the coprecipitation show

that V^{4+} is occupying a substitutional site, whereas the V(V)-doped TiO_2 , produced by the absorption method, showed poorly resolved spectra reflecting the possibility that the vanadium ions are not substituting into the TiO_2 lattice but exist on the surface.

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Preparation of PVC films

Poly(vinyl chloride) (1 g) was dissolved in HPLC grade tetrahydrofuran (20 cm^3) and the corresponding amount of modified TiO_2 pigment added (4 % loading in this case). The solution was then sonicated/stirred for approximately 1 h. Thin films (100 -150 μm) were prepared by pouring the solution into disposable aluminium trays (area = 8.55 cm^2) and allowing the solvent to evaporate. The weight of the resulting disc was then obtained (four decimal point balance) and recorded. From these data the thickness could be obtained by using the known area, weight and density of the PVC film. The thickness was then verified by analysing the film under an Olympus BH2 scanning optical microscope. The IR spectra were recorded and samples chosen for size according to their relative absorbances at 2913 cm^{-1} . The films were then irradiated in a QUV weatherometer (Q Panel Company) equipped with 8 UV_B 300 W bulbs at a temperature of 318 K.

20 UV irradiation equipment

A Q Panel QUV accelerated weatherometer was used. The device is essentially an UV irradiation tank. 8 fluorescent bulbs (300 W), selected as UV_B wavelength, are fitted inside the apparatus and a moisture bath can also be used to force harsh conditions. Thin film samples are mounted onto the plates and placed on the sides of the instrument. The light intensity delivered within the QUV weatherometer was determined using the potassium ferrioxalate system. The intensity at the side of the instrument was calculated to be 1.82×10^{17} quanta/s.

IR absorption spectra were recorded using a Perkin-Elmer 1000 spectrophotometer (range $3200\text{ cm}^{-1} - 400\text{ cm}^{-1}$). Resolution was predetermined at 4 cm^{-1} . The appearance of a carbonyl peak at 1718 cm^{-1} was monitored and calculated. The appearance of this peak over time was recorded and normalised with respect to the CH band at 2913 cm^{-1} to produce the "carbonyl index".

The results for the effect of addition of Mn and V to TiO_2 upon the photodegradation of PVC film is shown in Figures 1 to 3. "1% Mn (Co)" is Mn-doped TiO_2 made by the coprecipitation method and "1 % Mn (A)" is made by the absorption method; similar comments apply to V-doped materials. The protection factor was calculated after 500 h by comparison of the carbonyl indices of the doped samples with that of the undoped sample.

In Figure 1, the 1 % Mn (coprecipitation method) sample is $\sim 9\%$ more effective than the undoped TiO_2 at protecting the PVC film whereas the 1% Mn (absorption method) is $\sim 23\%$ more effective. In Figure 2 the 1 % V (coprecipitation method) sample is $\sim 20\%$ less effective than the undoped TiO_2 at protecting the PVC film whereas the 1 % V (absorption method) is $\sim 12\%$ more effective. In Figure 3 the 1 % V (coprecipitation method) sample is $\sim 6\%$ less effective than the undoped TiO_2 at protecting the PVC film whereas the 1% V (absorption method) is $\sim 6\%$ more effective.

CLAIMS

1. A composition which comprises an amount of one or more organic or inorganic components which are photosensitive and/or which are degraded by another ingredient of the composition and an amount of TiO_2 and/or ZnO which has been doped at least on or in a surface thereof with one or more other elements.
2. A composition according to claim 1 which has a rate of deterioration of a UV light-sensitive physical factor at least 5% less than that of a composition having the same formulation except that it does not contain the said TiO_2 and/or ZnO which has been doped with a second element.
3. A composition according to claim 1 or 2 wherein the dopant is manganese, selenium, iron, cerium, vanadium or chromium.
4. A composition according to claim 3 wherein the dopant is manganese.
5. A composition according to any one of the preceding claims wherein the dopant is present in an amount from 0.05% to 10 mole %.
6. A composition according to claim 5 wherein the dopant is present in an amount from 0.5 to 2 mole % by weight.
7. A composition according to any one of the preceding claims which contains doped titanium dioxide.
8. A composition according to any one of the preceding claims wherein the titanium dioxide is in rutile form.
9. A composition according to any one of the preceding claims which contains doped ZnO .
10. A composition according to any one of the preceding claims which comprises 0.5 to 20 mole % by weight of the doped TiO_2 or ZnO .
11. A composition according to any one of the preceding claims wherein the doped material has a particle size from 1 to 100 nm.
12. A composition according to claim 2 wherein the physical factor is tensile strength.
13. A composition according to claim 2 wherein the physical factor is colour.

14. A composition according to any one of the preceding claims which comprises TiO_2 and/or ZnO which has not been doped.

15. A composition according to claim 14, wherein the said TiO_2 and/or ZnO is present as pigment.

5 16. A composition according to any one of the preceding claims wherein the polymeric material is thermoplastic.

17. A composition according to any one of claims 1 to 15 wherein the polymeric material is thermosetting.

10 18. A composition according to any one of the preceding claims wherein the polymer is photosensitive.

19. A composition according to any one of the preceding claims which is in the form of a three dimensional article.

20. A composition according to any one of claims 1 to 18 which is in the form of a film.

15 21. A composition according to claim 20 which is in the form of a photographic film.

22. A composition according to any one of claims 1 to 18 which is in the form of a coating composition.

20 23. A composition according to claim 22 which is in the form of a paint or varnish.

24. A self-supporting polymeric composition intended to protect a composition adjacent thereto from the adverse effects of light which comprises TiO_2 and/or ZnO which has been doped at least in or on a surface thereof with one or more other elements or reduced ZnO .

25 25. A composition according to claim 24 wherein the TiO_2 and/or ZnO is present in a surface layer.

26. A composition according to claim 25 wherein a non-surface layer thereof is not wood.

30 27. A composition according to claim 25 or 26 wherein a non-surface layer thereof is synthetic.

28. A varnish composition which comprises TiO_2 and/or ZnO which has been doped at least in or on a surface thereof with one or more other elements or reduced ZnO .

29. A composition according to any one of claims 24 to 28 which has one
5 or more of the features of claims 2 to 23.

30. A composition according to claim 1, 24 or 28 substantially as hereinbefore described.

31. Use of a surface doped TiO_2/ZnO as defined in any one of claims 1 to 30 to reduce the concentration of one or more light stabilisers in a polymeric
10 composition.

32. Use of a surface doped TiO_2/ZnO as defined in any one of claims 1 to 30 to reduce the rate of deterioration of a light-sensitive physical factor in a polymeric composition.

33. A method of improving stability of a physical factor of a polymeric
15 composition, which comprises one or more components which are photosensitive and/or are degraded by another ingredient of the composition which comprises incorporating into the composition a surface doped TiO_2/ZnO as defined in any one of claims 1 to 30.

ABSTRACT

IMPROVED POLYMERIC COMPOSITION

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A polymeric composition is described which comprises an amount of one or more organic or inorganic components which are photosensitive and/or which are degraded by another ingredient of the composition and an amount of TiO_2 and/or ZnO which has been doped at least in or on a surface thereof with a second element.



Figure 1

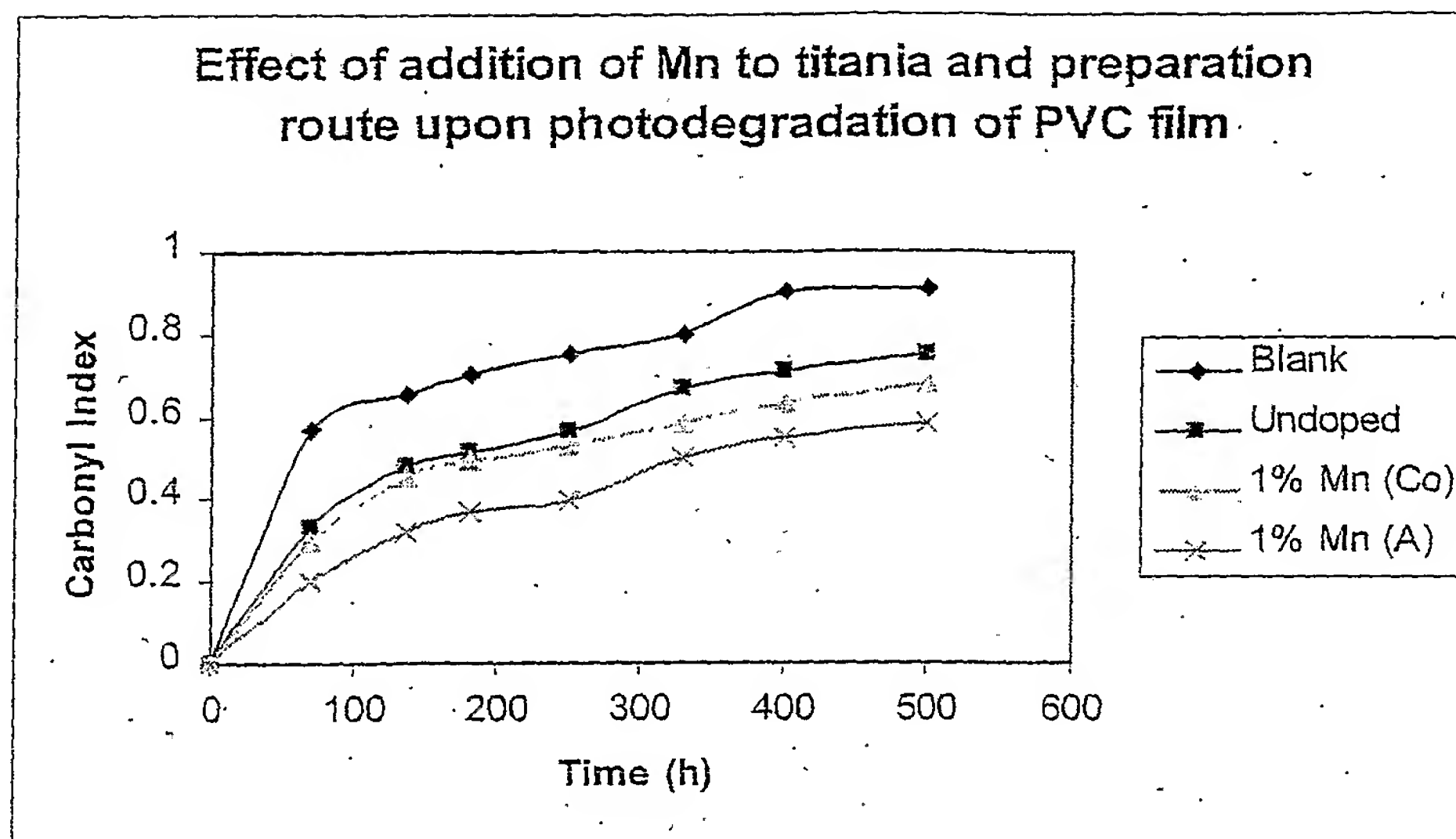


Figure 2

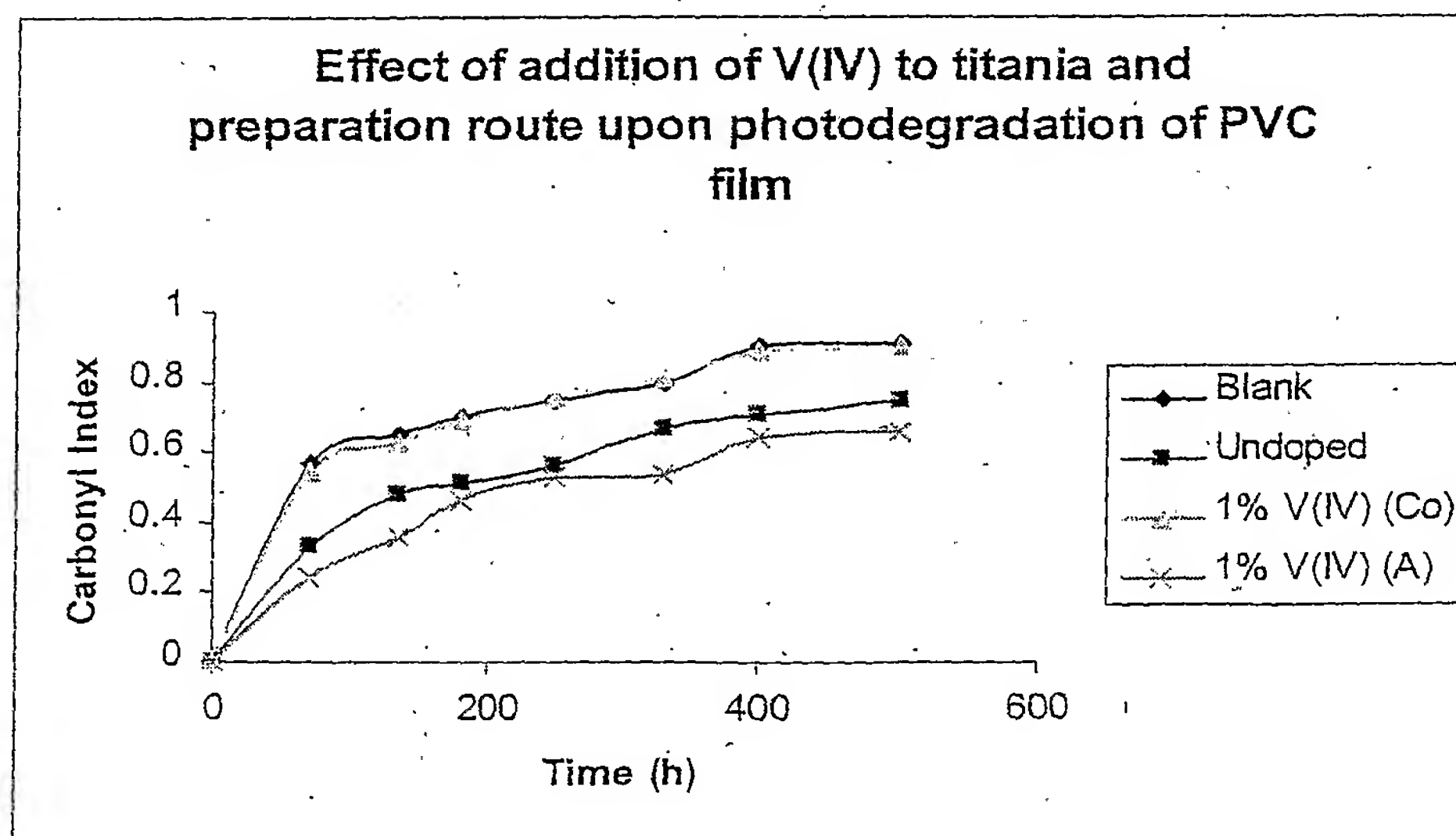




Figure 3

